continue to move upward to the polymeric mordant layer where they form the positive color image. The titanium dioxide acts to prevent further exposure of the film outside the camera and also serves as the white background for the positive image. This system uses a positive working chemistry and a negative emulsion.

Kodak[7] has introduced an instant color process that uses a negative working chemistry and a reversal emulsion. In this system the dyes are attached to immobile carriers, not dye couplers. The activator fluid is highly alkaline and causes the release of the dye from the carrier. To produce a positive dye image specially developed silver halides are used with nucleating agents in each light-sensitive layer. The sensitivity centers in the silver halide crystals attract the photoelectrons when exposed to light. No latent image sites are formed on the surface of the exposed crystals and the unexposed crystals form surface-latent image sites because they have weak internal attractions for photoelectrons. The dyes are released at the point where the development occurs and thus do not migrate as in the Polaroid system.

MANUFACTURE OF FILMS, PLATES, AND PAPERS

In the making of photographic films, plates, and papers, three distinct steps are carried out: (1) preparation of the light-sensitive emulsion, (2) manufacture of the base or support for the emulsion, and (3) coating of the emulsion on the base. Figure 7.3 gives a general representation of the manufacturing steps involved.

EMULSIONS. The so-called photographic emulsion is in reality not a true emulsion but rather a suspension of finely divided silver halide grains in gelatin. The gelatin serves as a mechanical binder, a protective colloid, and a sensitizer for the halide grains.[8] The manufacture of the emulsion usually requires ripening and addition of chemicals to control speed, contrast, stability, fog, and sensitivity to desired wavelengths. Hardeners are also added to improve the thermal stability and mechanical durability of the gelatin. In the manufacture of emulsions for color photography, other additions such as dyes and dye couplers are made.

Silver halides are sensitive only to wavelengths shorter than 500 nm (the ultraviolet, violet, and blue wavelengths). When nonsensitized silver halides are used, the resulting ordinary emulsion reproduces blues as light and greens and reds as dark. Dyes can be added to increase the halide sensitivity (spectral sensitivity). If the sensitivity is increased to 600 nm (the green wavelengths), the resulting halide emulsion is known as *orthochromatic* and reproduces blues and greens as light and red as dark. When additional dye is added to sensitize the halide to 700 nm (red wavelengths), the *panchromatic* emulsion reproduces good tone values of all the colors.

Table 7.2 shows the types of chemicals used in preparing photographic emulsions. The halide used influences the speed of the emulsion: Ag_2Br_2 and small amounts of Ag_2I_2 produce fast emulsions, while for slower emulsions, Ag_2Cl_2, Ag_2Br_2, and Ag_2ClBr are used. The finished emulsion generally consists of 35 to 40% silver halide, 65 to 60% gelatin, and small amounts of the special-use chemicals.

The silver halide is precipitated in the presence of gelatin by treating silver nitrate with the appropriate potassium halide. The gelatin acts as a protective colloid and allows suspension of the microcrystalline silver halide. These microcrystals produce a very "slow" emulsion

[7]Kodak Details Chemistry of Instant Film, *Chem. Eng. News* 54 (26) 32 (1976).

[8]Duffin, op. cit.
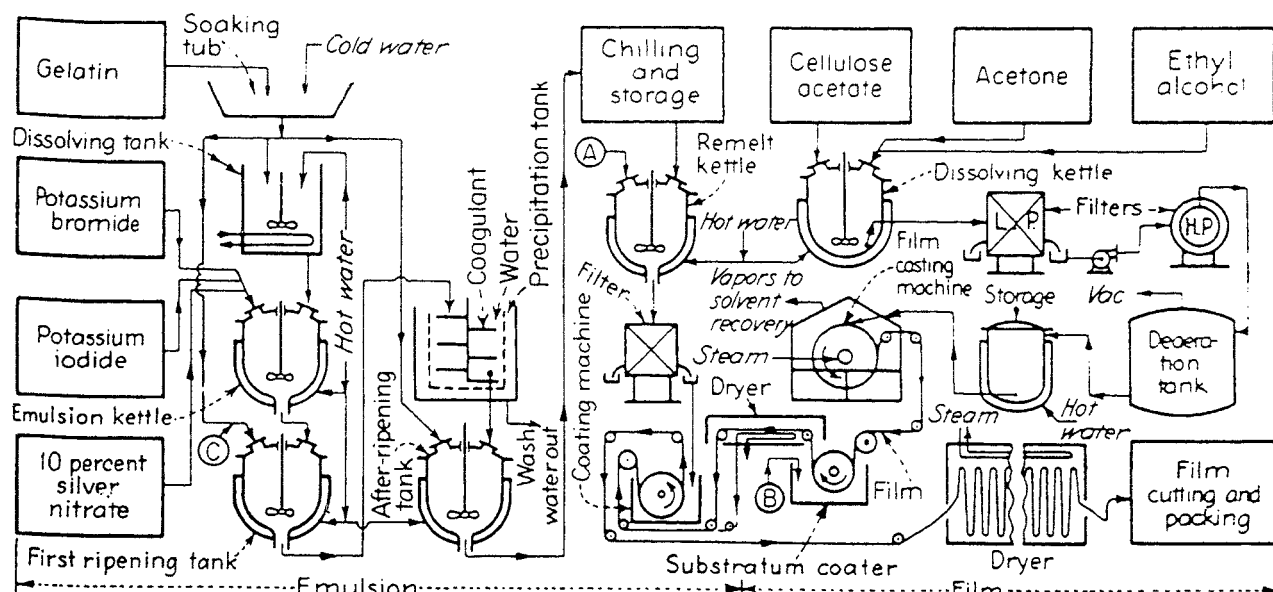
In order to produce 1000 m² of film, the following materials (in kilograms) are required (the solvents are mostly recovered):

Potassium bromide	110	Cellulose acetate	220
Potassium iodide	0.29	Glycerin	245
Gelatin	39.2	Ethyl alcohol	297
Silver nitrate	9.8	Acetone	579

Fig. 7.3. Flowchart for the production of photographic film. Extreme cleanliness must be practiced and an appropriate safety light provided after the silver halide has been formed. NOTES: A, Chrome alum, preservative (phenol or thymol), saponin, KBr, and sensitizing dyes are added here. B, Gelatin and solvent used for substratum coating. C, Gelatin added at close of ripening period.

Table 7.2 Chemicals Used in Preparing Black-and-White Photographic Emulsions

Use	Chemical	Action
Mechanical, protective binder	Gelatin	Base in which to form halide dispersion
Image formation	Silver halides	Forms latent image site when exposed to light
Chemical sensitization	Thiosulfates and thiourea	Increases light sensitivity (speed)
Chemical sensitization	Stannous chloride and sodium sulfite	Reducing agents to increase sensitivity
Chemical sensitivity	Gold salts—as ammonium aurothiocyanate	Increases sensitivity
Stabilization	Triazoles, tetrazoles, or iminazoles	Stops chemical sensitization
Spectral sensitization	Cyanine dyes	Increases wavelength sensitivity
Hardeners	Aldehydes and chromium salts	Increases thermal stability and resistance to abrasion
Antifogging	Potassium bromide, benzimidazoles, benzotriazoles, and mercaptotetrazoles	Stabilizes chemical sensitization to prevent photographic fog
Uniform coating of emulsion on base	Surfactants	Controls surface tension of gelatin and acts as spreading agent

so a ripening process is necessary to allow larger grains to be formed. The small crystals, being more soluble than the large ones, tend to dissolve and reprecipitate on the large crystals. The finished crystal size ranges from 0.1 to 0.3 μm.[9]

The ripened emulsion is leached with cold water to remove any soluble salts and then heated with a compound that will form silver sulfide specks at the grain surface. The sensitivity of the silver halide can be increased from 10 to 100 times by this process. If one silver atom out of 10^5 atoms is converted to silver sulfide, it is sufficient. For very sensitive film a small amount of a gold salt is added.

After the emulsion has been chemically sensitized, dyes are added to spectrally sensitize it so that it will reproduce good tones from all the wavelengths of visible light. Before coating the emulsion on the support, it is customary to add chrome alum or formaldehyde as a hardening agent. Phenol or thymol may be introduced to prevent growth of mold or bacteria. The addition of KBr at this stage aids in the prevention of fog. The introduction of amyl alcohol or saponin serves to depress the surface tension of the liquid emulsion, facilitating uniform foam-free spreading on the support.

EMULSION COATING. The sensitized emulsion may be coated on glass, plastic, or paper depending upon the end use. Glass provides the most dimensionally stable support, but its weight and fragility make it unsuitable for any use but precision photography. Clear plastic supports are the most widely used in modern photography while paper is used for print materials.

Various methods of coating the support with the emulsion are in use. Usually the support is moved on rollers past the coating station. The liquid emulsion may be in a trough, and the support is brought in contact with the surface of the emulsion. Excess emulsion is removed by air jets or by a knife edge. Alternately, the emulsion may be spread over the support by pumps or gravity flow from hoppers. The coated support is cooled to gel the emulsion and then dried to remove most of the water. The finished layer is only about 10 percent of the original thickness.

The finished product consists of several separately applied emulsion layers. An intermediate layer is used to prevent stray light from reflecting back into the sensitized emulsion during exposure. A final coat of especially hardened gelatin is used for protection of the emulsion surface.

Color film requires many layers of emulsion, each one sensitive to one of the three colors (blue, green, and red). Some color films have more than six coatings. Each layer is applied separately and dried before the next one is applied, although the patent literature claims that up to six layers can be coextruded onto a ramp and then transferred to the film base without intermixing of the layers, which would be a catastrophe in the manufacture of color film.

SPECIAL APPLICATIONS OF PHOTOGRAPHY

PHOTOMECHANICAL REPRODUCTION FOR ILLUSTRATIONS.[10] Photography has found one of its most important applications in the reproduction of photographs on the printed page by means of printing inks. These processes may be classified as (1) *relief printing*, also referred

[9]*Focal Encyclopedia of Photography,* Focal, London, 1969.

[10]For brief technical descriptions of these processes, see CPI 2, p. 592.

; photoengraving, in which the raised portion of a plate receives the ink for transference
ie paper, and so-called *line* plates and *halftone* plates are used; (2) *intaglio* printing,
:h includes photogravure, rotogravure, and metal engraving, in which the relief printing
edure is reversed and the hollow regions of the plate or metal cylinder hold the ink; (3)
ographic printing, or lithography,[11] which makes use of the inability of a water-wet sur-
to take ink. The *offset printing process* utilizes lithographic plates which are particularly
table to illustrative work in color, and the usual separation negatives are used in their
aration.

lotopolymerization, or polymerization initiated by light, has the ability (as has silver
le photography) to amplify the effect of light enormously; the multiple effect, however,
rs simultaneously with exposure, rather than in a separate processing step. This method
been used extensively in the printing field. The Kodak Photo Resist process for making
engravings was introduced in 1954; it uses the cross-linking of a photopolymer system.
il photopolymer printing plates, which use photosensitive acrylic plastic bonded to
l, were marketed in 1960, and the time for making a plate has been reduced to ¼ h as
ared with 4 h needed for making a conventional metal engraving. A photopolymer
ing plate formed by the light-induced cross-linking of nylon has been described in the
ture.[12] In 1964 a process called *panography* was introduced—the first successful use of
to create a three-dimensional effect on a flat surface. A thin film of transparent plastic
rial, called Epolene, is applied to produce the effect, and a special press is used for the
:ss.[13]

OCOPYING.[14] Photographic copying of documents reaches back to the earliest days of
graphy. Although newer methods of photocopying have largely replaced the earlier
in which visible images are produced on exposure of prepared paper, some of these
ing-out processes are capable of producing exceptionally fine prints, and others afford
tain control over tone values unequaled by any other process. Several have been
bed by Neblette; among them are the silver, chromate, and iron processes. Herschel
oped the *blueprint process* in 1842, a method dependent on the ability of ferric ions to
luced to ferrous ions in the presence of organic matter under the influence of strong
Paper is coated with ferric ammonium citrate and potassium ferricyanide. When a line
ng is placed over the prepared paper and then exposed to light and treated with water,
oluble blue image is formed where the light reaches the paper; this image is in prussian
ferric ferrocyanide ($Fe_4[Fe(CN)_6]_3$). The cyanotype, or positive blueprint (where lines
ue and background light), uses a more radiation-sensitive ferric mixture and, processed
potassium ferricyanide solution, yields Turnbull's blue, ferrous ferricyanide
'e(CN)_6]_2$).

.839—the same year that two other milestones in photography were reached—Breyer
mented with silver halide–coated paper to copy pages from books. However, the first
sful document-copying device not requiring especially prepared originals was the Rec-
h, invented about 1900. Other projection photographic copying machines followed,
ing the Photostat, but all had their shortcomings. Contact-box printers were introduced

---

iginally, lithography meant engraving on stone and printing therefrom, a process not
urrently except for special work in small quantities.

iem. *Eng. News* 42 (30) 91 (1964).

aphic Advance, *Barron's*, May 25, 1964, p. 3.

T, 3d ed., vol. 20, 1982, p. 128, gives an excellent description of various processes.

in the 1930s, but they did not meet the demand for speed and easy operation. It was not until the *diffusion-transfer reversal process* was patented about 1940 that the revolution in copying methods began. These copying techniques are image-forming processes which create essentially full-sized copies of the original and should not be confused with office duplicating processes such as mimeographing, multilithing, or the newer adherography. Copiers reproduce directly from an original document, while duplicators reproduce through the use of an intermediate master.

The most widely used photocopying process is the *electrostatic process* invented by the Xerox company in 1937, but not commercially available until 1950. Figure 23.4 shows the essential details of this process. Because the electrically charged selenium is an integral part of the drum, plain paper can be used. The *Electrofax* process is similar to the *Xerox*, but it uses an electrically charged zinc oxide–coated paper instead of the selenium-coated drum.

Among other processes are (1) thermography, which uses the heat of infrared rays for exposure and requires that the original have carbon or a metallic compound in the text ink and thus cannot copy colored originals; (2) dry silver process (electrophotographic); (3) electrolytic process; and (4) wet transfer processes. Table 7.3 lists some of the most popular processes.

MICROFILMING. Microphotography is the art of making miniature photographic facsimiles of original materials. It is currently used by insurance companies, banks, and engineers for commercial records in active use or for security purposes. This method is also used by libraries
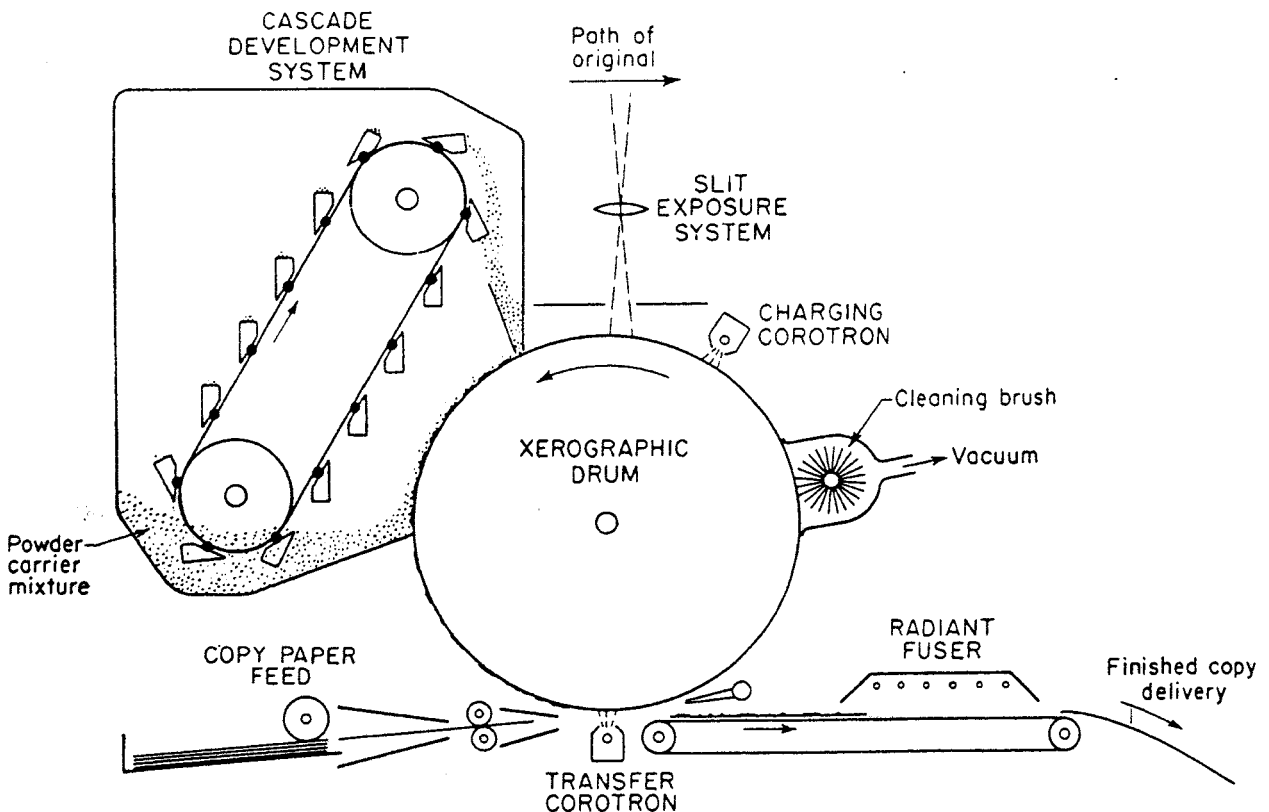

Fig. 7.4. Automatic xerographic copying equipment makes use of the photoconducting property of amorphous selenium plated on the xerographic drum. The selenium holds a positive electrostatic charge in the dark (but allows it to be dissipated when exposed to light). The revolving drum is sensitized through exposure by contact, by projection, or in a camera. The latent image is on the positively charged drum, which attracts the negatively charged black-powder resinous carrier mixture. This resinous pigment is then heated and passed from the drum to the copy paper on which the image is fused.

Table 7.3 Office Copying Processes

Process	Manufacturer	Paper	Copies per minute	Copies Colors	Size Reduction
Electrostatic	IBM	Plain	75	Yes	Yes
Xerographic	Xerox	Plain	10–75	Yes	Yes°
Electrophotographic	Kodak	Plain	70	Yes	Yes°
Xerographic	3M	Plain	25	Yes	No
Electrostatic	3M	Coated	15	Yes	No
Dry toner–dual component	Sharp	Plain	25	Yes	No
Liquid-toner transfer	Savin	Plain	30	Yes	No
Thermal	Heyer	Coated	8–15	No	No
Electrofax	Albin Ind.	Coated	13	Yes	No

°Some models can reduce size.
SOURCE: *The Office* 94 (1) 121 (1981).

for historical records and newspapers in permanent files to conserve space. Such uses have brought about a revolution in *microforms*. Microfilm normally has a reduction of 12 to 22 diameters of the original copy. The resolving power is well over 100 lines/mm, and emulsions capable of resolving 500 lines/mm are being developed. The film itself has a slow-speed panchromatic silver emulsion on a cellulose acetate base. Duplication of the microfilm negative can be by contact printing for a positive reproduction or by negative-to-negative printing. *Microfiche* is the name applied to single-sheet forms of microfilms.

Kalvar film is used for positive copies. When it is exposed, gas bubbles of nitrogen are created which scatter the light. On heat development, the nitrogen develops high pressure which blows air sacs that are 0.5 to 2 μm in diameter. Ultraviolet light stabilizes the compound and the air sacs then scatter the light when the film is projected. It is often used for microfilm (either roll or sheet) duplication.

SELECTED REFERENCES

Clerk, L. P.: *Photography, Theory and Practice*, D. A. Spencer (ed.), Focal, London, 1972.
Cox, R. J.: *Photographic Processing*, Academic, New York, 1973.
Cox, R. J.: *Photographic Sensitivity*, Academic, New York, 1973.
Duffin, G. F.: *Photographic Emulsion Chemistry*, Focal, London, 1969.
Focal Encyclopedia of Photography, Focal, London, 1969.
James, R. W.: *Photographic Emulsions*, Noyes, Park Ridge, N.J., 1973.
James, T. H.: *Theory of the Photographic Process*, 4th ed., Macmillan, New York, 1977.
Mason, L. F. A.: *Photographic Processing Chemistry*, 2d ed., Wiley, New York, 1975.
Neblette, C. B.: *Handbook of Photography and Reprography*, 7th ed., Van Nostrand Reinhold, New York, 1977.
Woodlief, T. (ed.): *SPSE Handbook of Photographic Science and Engineering*, Wiley, New York, 1973.

Chapter 8

Surface-Coating Industries

Products of the surface-coating industries are essential for the preservation of all types of architectural structures, including factories, from ordinary attacks of weather. Uncoated wood and metal are particularly susceptible to deterioration, especially in cities where soot and sulfur dioxide accelerate such action. Aside from their purely protective action, paints, varnishes, and lacquers increase the attractiveness of manufactured goods, as well as the aesthetic appeal of a community of homes and their interiors. Coatings that are used to cover buildings, furniture, and the like are referred to as trade sales or architectural coatings in contrast to industrial coatings which are used on materials being manufactured. Industrial finishes are applied to a wide variety of materials, such as metal, textiles, rubber, paper, and plastics, as well as wood. Architectural coatings are usually applied to wood, gypsum wallboard, or plaster surfaces.

HISTORICAL. The surface-coating industry is indeed an ancient one; in fact, Noah was told to use pitch within and without the Ark. The origin of paints dates back to prehistoric times when the early inhabitants of the earth recorded their activities in colors on the walls of their caves. These crude paints probably consisted of colored earths or clays suspended in water. The Egyptians, starting very early, developed the art of painting and by 1500 B.C. had a large number and wide variety of colors. About 1000 B.C. they discovered the forerunner of our present-day varnishes, usually naturally occurring resins or beeswax were the film-forming ingredient. Pliny outlined the manufacture of white lead from lead and vinegar, and it is probable that his ancient procedure resembles the old Dutch process.

USES AND ECONOMICS. The manufacture of surface coatings is big business with sales near $10,000 million yearly. No one company has over 10 percent of the market, and there are between 1000 and 1200 companies vying for business. Table 24.1 shows the current and projected size of the market. More than 70 percent of the trade sale paints are water-based.

PAINTS[1]

Historically, surface coatings have been divided into paints (relatively opaque solid coatings applied as thin layers, whose films were usually formed by polymerization of a polyunsatu-

---

[1]ECT, 3d ed., vol. 16, 1982, pp. 742–761; Weismantel, *Paint Handbook*, McGraw-Hill, New York, 1981.

Table 8.1 Production of Coatings in the United States
(in millions of liters and dollars)*

	1979		1995	
	Volume	Value	Volume	Value
Trade sales (architectural)	1695	$3202	2440	$9 325
Industrial	1375	2545	2070	9 055
Special purpose	510	1303	1040	5 440
Total	3580	7050	5550	24 820

°Includes powder coatings

SOURCE: *Chem. Bus.*, October 19, 1981, p. 11

rated oil), varnishes (clear coatings), enamels (pigmented varnishes), lacquers (films formed by evaporation only), printing inks, polishes, etc. These classifications have been most useful in the past, but the introduction of plastic resins into the industry has made such classes ..... relatively meaningless.

Table 8.2 lists the most important types of ingredients currently used in surface coatings.

CONSTITUENTS. Liquid paint is a dispersion of a finely divided pigment in a liquid composed of a resin or binder and a volatile solvent. The liquid portion is known as the vehicle. The constituents of paints are outlined in Tables 24.2 and 24.3. The pigment, although usually an inorganic substance, may also be a pure, insoluble organic dye known as a toner or an organic dye precipitated on an inorganic carrier such as aluminum hydroxide, barium sulfate, or clay, thus constituting a lake. Pigment extenders, or fillers, reduce the cost of paint and frequently increase its durability. The function of pigments and fillers is not to provide simply a colored surface, pleasing for its aesthetic appeal, important as that may be. The solid particles in the paint reflect many of the destructive light rays, and thus help to prolong the life of the paint. In general, pigments should be *opaque* to ensure good covering power and chemically inert to secure stability, hence long life. Pigments should be nontoxic, or at least of very low toxicity, to both the painter and the inhabitants. Finally, pigments must be wet by the film-forming constituents and be of low cost. Different pigments possess different covering power per unit weight.

Although oils often serve as part of the vehicle for the carrying of pigments, their chief function is to form, or to help form, the protective film and to plasticize it. Without film-forming materials, the pigments would not cling to the surface. Oil paint films are formed

Table 8.2 Paint Constituents

Vehicles
A. Nonvolatile
    1. Solvent based: oils and/or resins plus driers and additives
    2. Lacquers: cellulosics, resins, plasticizers, additives
    3. Water based: styrene-butadiene, polyvinyl acetate, acrylic, other polymers and emulsions copolymers plus additives
B. Volatile
    Ketones, esters, acetates, aromatics, aliphatics

Pigments
  Opaque, transparent, special-purpose types

SOURCE: Weismantel, *Paint Handbook*, McGraw-Hill, New York, 1981, p. 3-3

by the "drying" of various unsaturated oils. These are further described in Chap. 28. The drying is a chemical change involving oxidation and polymerization; it is hastened by pretreatment of the oil and by adding driers, or catalysts, predominantly heavy metallic soaps, which are oxygen carriers usually soluble in oil. These driers need be used only in small amounts (1 to 2% by weight). Reactive oils, such as linseed, soybean, castor, safflower, and tung, are used.

The film-forming nonvolatile portion of the vehicle may be a synthetic resin instead of a drying oil. These synthetic drying oils are known as alkyds and may be made from fatty acids or oils, polybasic acids, and polyhydric resins. Many paints contain both natural and synthetic drying oils. The drying or the hardening of these oils involves chemical reactions, which are rather complex but include oxidation as the initiating step. Some polymerization also occurs and much cross-linkage. Oils which dry to a film possess olefinic unsaturation. For example, the acids of linseed oil contain about 9% saturated acids (palmitic and stearic), 19% oleic acid, 24% linoleic acid, and 48% linolenic acid. In drying, these oils first absorb oxygen from the air, forming peroxides or hydroperoxides at the olefinic bonds. These still-liquid products partly decompose, giving volatile oxidation products, but mainly change in the next stage of the reactions by cross-linkages into the solid, though still elastic, films through colloidal aggregation. In the case of linseed oil, the solid, insoluble, elastic film is called linoxyn. Such films are not permanent, since the chemical reactions continue, though at a much slower rate, until after the course of years the film is entirely destroyed. Light, particularly ultraviolet, catalyzes these reactions, and one of the functions of the pigment in surface coatings is to reflect the light and thus help preserve the film.

Drying oils are seldom used unmodified.[2] They may be improved in a number of different ways by (1) the action of driers (i.e., drying catalysts or promoters), (2) oil bodying, (3) fractionation and segregation, (4) isomerization or conjugation, (5) dehydration, and (6) other carbon double-bond reactions. There are also copolymer oils, poly alcohols such as polypentaerythritol, oil-modified alkyds, and synthetic oils. Bodied oils vary with the oil, but generally have better drying, wetting, and color retention properties than unbodied oils. Bodying is an oxidation reaction and may be achieved either by heating in kettles or by blowing air in fine bubbles through the oils at 100 to 200°C for several hours. Solvent or liquid-liquid extraction separates the drying constituents of an oil from the nondrying constituents. The isomerization of paint oils, especially popular for linseed and soybean oils, involves partial rearrangement of the isolated, nonconjugated double bonds into more reactive conjugated positions upon heat treatment with catalysts, such as certain metal oxides, activated nickel, or SO_2. Dehydration, at present, is applicable only for castor oil and is achieved by heating the oil in a vacuum in the presence of dehydrating catalysts such as alumina, fuller's earth, silica gel, H_3PO_4, or H_2SO_4.

In emulsion-base paints, the film-forming materials are the various latices with or without other additions. Film formation takes place largely through coalescence of dispersed resin particles to form a strong continuous film. The vehicle for this class of paints is an emulsion of binder in water; the binder may be oil, an acrylic or polyvinyl acetate resin, or another emulsifiable binder. Although water-thinned paints date back to antiquity, they were not commercially important until casein-based paints were developed about 1925. Their phenomenal growth is indicated by the large increase in U.S. production. Resin-emulsion paints have been widely used since World War I, but latex-based paints, introduced commercially in 1948, have had spectacular growth; more than 70 percent of interior paint sales are this type. This type of paint was developed to meet demands for greater ease of application, quick

---

[2]Mattil, Short Course on Drying Oils, *J. Am. Oil Chem. Soc.* 36 477 (1959).